

09/830830

I/PRTS

WO 01/16384

PCT/IL00/00513

JC08 Rec'd PCT/PTO 30 APR 2001

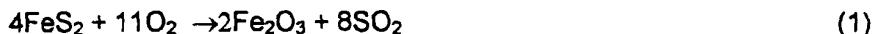
SULFATISATION PROCESS FOR METAL EXTRACTION FROM SULFIDE ORES

**Technical Field**

The present invention relates to the field of hydrometallurgical processing of sulfide metal-containing ores and sulfide waste (dump sulfide tails) obtained after separation of sulfide concentrates of zinc, copper etc. by flotation aimed at production of metal sulfates, oxides, and other compounds as well as sulfuric acid, wherein said metal is selected from the group consisting of iron, copper, zinc, nickel, cobalt and manganese.

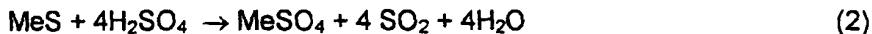
**Background Art**

The method for calcination of iron sulfides, pyrite, marcasite etc. at a high temperature  $\geq 900^{\circ}\text{C}$  according to the reaction:



is known. The escaping gas is converted to sulfuric acid, and a calcine ( $\text{Fe}_2\text{O}_3$ ) is used for production of various iron compounds or applied in ferrous metallurgy to obtain metal iron. However, because of a high residual content of sulfur in the calcine, its application in metallurgy is limited and it is usually dumped. [Short Chemical Encyclopedia, Moscow, 1979].

There is known a method of sulfatization of sulfide materials by their treatment with concentrated sulfuric acid at  $200^{\circ}\text{C} - 300^{\circ}\text{C}$  [Pat US 1895811, 1933; L.E.Makovezky, H.Morgan]. This process is described by a reaction:



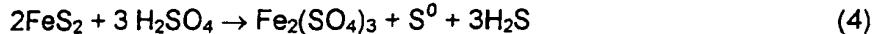
where Me - Fe, Ni, Zn, Cu etc.

However, the largest extent of sulfatization (78.4%) of pyrite ( $\text{FeS}_2$ ) was achieved at  $200^{\circ}\text{C}$ , the sulfatization extent of copper sulfides was lower.

With temperature increase to  $300^{\circ}\text{C}$  the reaction of pyrite sulfatization proceeds as follows:



At a temperature  $300^{\circ}\text{C}$  sulfuric acid behaves as a strong oxidizer and a portion of iron is oxidized to Fe(III) [S.S.Naboiuchenko, V.I.Smirnov "Hydrometallurgy of copper", Moscow, "Metallurgiya", 1974]:



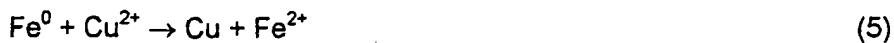
There exists a method for sulfatization of zinc and copper sulfides by their dissolving in sulfuric acid of a high concentration (45 - 70%) at a temperature below the boiling point of these solutions (for 45% H<sub>2</sub>SO<sub>4</sub> - ≤130°C; for 70% H<sub>2</sub>SO<sub>4</sub> - ≤140°C). Under these conditions zinc sulfate was obtained (ZnSO<sub>4</sub> · H<sub>2</sub>O), sulfatization of copper and iron sulfates proceeded incompletely [Pat. US 5711922, Jan.27.1998; O'Brien, Robert N.].

Sulfide ores and concentrates can be also treated with a mixture of sulfuric and nitric acids at 110 - 170°C. Sulfuric acid concentration is 40 - 65%. The amount of nitric acid required for sulfatization is 0.5 - 3.0 moles of HNO<sub>3</sub> per 1 mole of sulfides which are contained in the treated material [Pat. US 5484579, Jan.16, 1996; O'Brien, Robert N.]. This technology does not provide a complete sulfatization of metal sulfides as well. In addition a complicated problem of utilization of gases SO<sub>2</sub> and SO<sub>3</sub>, which contain nitrogen oxides arises.

All the patents mentioned above deal with a complicated and yet unsolved problem of separation of admixtures of sulfates of such metals as Al, Cu, Zn, Ni etc. from iron sulfates.

Usually the solution of metal sulfates obtained after sulfatization and leaching is oxidized with oxygen of air or by other methods in order to convert Fe<sup>2+</sup> to Fe<sup>3+</sup>, then the solution is adjusted to pH=2, iron precipitates as Fe(OH)<sub>3</sub>, and the admixtures remain in solution. To obtain iron (III) sulfate, iron hydroxide is again dissolved in sulfuric acid. Extraction of admixtures from the sulfuric acid solution is a complicated problem.

If the solution obtained after sulfatization contains a large amount of copper, the method of cementation with iron scrap is applied. It is described by the following reactions:



Copper precipitates as a metal powder, and iron converts to its bivalent form FeSO<sub>4</sub>, all admixtures, except for copper, are in solution with iron. Isolation of pure iron sulfate from this solution is a large technological problem.

The present invention is aimed at the development of the method for processing sulfide ores and concentrates, in particular pyrite, performed at lower temperatures than pyrite calcination and which results in the production of highly

pure iron sulfates without using additional amounts of reagents for neutralization of strongly acidic solutions.

**Disclosure of the Invention.**

Thus, according to the present invention, there is now provided a hydrometallurgical process for producing metal-containing sulfide ores and concentrates, comprising reacting said metal-containing sulfide with concentrated sulfuric acid at a temperature of between about 300°C and 400°C in the presence of oxygen to produce a solid metal sulfate product and a gaseous product which is primarily SO<sub>3</sub>, wherein said metal is selected from the group consisting of iron, copper, zinc, nickel, cobalt and manganese.

In preferred embodiments of the present invention said metal is iron.

In preferred embodiments of the present invention said metal sulfate product is then leached with a dilute solution of sulfuric acid, having a concentration of between 5% and 35% to extract iron values therefrom and to form an iron-containing solution.

In especially preferred embodiments of the present invention said SO<sub>3</sub> gaseous product formed from said reaction is subsequently combined with said metal-containing solution to raise the concentration of sulfuric acid in said solution to about 35% to 50% and to effect the precipitation of said metal from said solution.

Thus, in a most preferred embodiment of the present invention the milled sulfide ore, particularly pyrite FeS<sub>2</sub>, is mixed with concentrated (98.3%) sulfuric acid and calcined in a furnace at a temperature about 338.8°C and at a constant blowing of air or air enriched with oxygen.

A temperature 338.8°C is the maximum temperature for sulfuric acid solutions, this is the boiling temperature of azeotrope containing 98.3% of H<sub>2</sub>SO<sub>4</sub>. With a temperature rise pyrite and other sulfides much better interact with sulfuric acid. In addition, an application of oxygen of air results in the following reaction for this process:



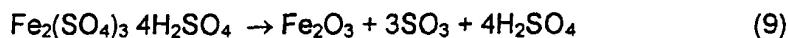
The product resulted from sulfatization was leached in diluted solution of sulfuric acid ( $\leq 36\%$  at  $\approx 90 - 100^\circ\text{C}$ ). The extraction of iron to solution was 95%, of them 92.15% was in a form of Fe(III).

After leaching the unsolved cake, containing SiO<sub>2</sub>, CaSO<sub>4</sub>, aluminosilicates etc, was separated from the solution by filtration. Then gas SO<sub>3</sub>, formed in the sulfatization process, was blown through the solution so that to increase the concentration of sulfuric acid to 42% (Precipitation I)



At such a concentration of sulfuric acid 89.1% of iron was salted out (precipitated) as highly pure Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · 4H<sub>2</sub>SO<sub>4</sub>. This product was filtered off, and gas SO<sub>3</sub> was continuously blown through the solution to a concentration of sulfuric acid 43.0 - 43.2% H<sub>2</sub>SO<sub>4</sub>. During this process rather unpure crystals of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> precipitated (Precipitation II), which were returned to stage Precipitation I for further purification. Solutions after Precipitation II were saturated with SO<sub>3</sub> to H<sub>2</sub>SO<sub>4</sub> concentration 98.3%. At such a concentration of sulfuric acid practically all the admixtures precipitated (Precipitation III), filtered off and used for production of a concentrate of nonferrous metals. The sulfuric acid composition corresponded to that of sulfuric acid produced for sale. The acid was partially returned to the head of the process for sulfatization, partially it was used as a product ready for sale.

Iron sulfate crystals obtained after Precipitation I were decomposed at ≈700°C



Gas SO<sub>3</sub> formed in this process is used at one of the precipitation stages. The admixtures after precipitation III are sulfates of such metals as Al, Ti, Zn and others. After filtration they were decomposed at 600°C -700°C:



The escaping gas SO<sub>3</sub> was also used for precipitation, and the residual formed after calcination is a concentrate of nonferrous metal oxides. The composition of this concentrate depends on the composition of a raw material used.

The invention will now be described in connection with certain preferred embodiments with reference to the attached flow sheet and the following examples so that it may be more fully understood.

With specific reference now to the examples, it is stressed that the particulars discussed are by way of example and for purposes of illustrative discussion of the preferred embodiments of the present invention only and are presented in the cause of providing what is believed to be the most useful and readily understood

description of the principles and conceptual aspects of the invention. It is not intended, however, to limit the invention to these particular embodiments. On the contrary, it is intended to cover all alternatives, modifications and equivalents as may be included within the scope of the invention as defined by the appended claims. Thus, the following examples which include preferred embodiments will serve to illustrate the practice of this invention, it being understood that the particulars shown are by way of example and for purposes of illustrative discussion of preferred embodiments of the present invention only and are presented in the cause of providing what is believed to be the most useful and readily understood description of formulation procedures as well as of the principles and conceptual aspects of the invention.

#### Description of Preferred Embodiments

##### Example 1.

Sulfide waste, which was obtained from sulfide ore after separation of zinc and copper concentrates by flotation, is used as a raw material. Sulfide waste has the following composition: Fe - 34.0%; Al - 3.34%; Ca 3.37%; Mg - 3.08%; Ti - 0.72%; Zn - 0.21%; Pb - 0.03%; Cu - 0.15%; Mn - 0.07%; Ni - 0.003%; Co - 0.015%; V - 0.02%; Na - 0.023%; K - 0.14%; As - 0.04%; Ag - 3.2  $10^{-4}$ %; S - 22.6%; Si - 4.97%; H<sub>2</sub>O - 9.1%, and the following fraction analysis:

Particle size, micron	Fraction content, %
+350	0.90
+210	4.82
+99	16.07
+75	14.63
+44	34.13
-44	29.45
In total	100%

A sample of sulfide waste was milled in a ball mill to a size -75 micron -100%, then it was mixed at room temperature with concentrated sulfuric acid in a ratio 1:0.94 by weight. Mixing was made during 30 min., then the mixture obtained was loaded to a tube furnace, where the sulfatization process occurred at 338°C. Air was blown during the sulfatization process. The amount of air required was 1900 l/1 kg of sulfide waste, that is 200% of the amount theoretically required according to

reaction (7). Sulfatization time is 2 hours. Gas SO<sub>3</sub> escaping at sulfatization is forwarded to scrubbers for precipitations I, II or III. The product resulted from sulfatization was loaded to a reactor for leaching (2.4 litters of 20% H<sub>2</sub>SO<sub>4</sub> per 1 kg of the sulfatized product). Leaching was performed at a temperature 90 - 100°C for 2 hours at constant stirring, the pulp was filtered on a vacuum filter, the solution goes in a scrubber for precipitation of pure iron (III) sulfate (Precipitation I), and the cake is washed with water on a filter. Sulfuric acid was added to wash water to a concentration ≈20% and used for leaching of the following portion of the sulfatization product.

The cake after washing contained 0.1% H<sub>2</sub>SO<sub>4</sub> free; 11.5% CaSO<sub>4</sub>; 10.65% SiO<sub>2</sub>; Al<sub>2</sub>O<sub>3</sub>; TiO<sub>2</sub> and other admixtures. It was neutralized by slaked lime [Ca(OH)<sub>2</sub>] that resulted in an increase in CaSO<sub>4</sub> content to 33-34%. This product can be used as a building material.

After leaching the solution contained 95.8g/l Fe (342.8 g/l Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>), it was used for Precipitation I. The crystals obtained after Precipitation II were returned to this solution.

Precipitation I was made at room temperature by blowing SO<sub>3</sub> (gas) in order to increase the sulfuric acid concentration in solution to 42%. At such a concentration of sulfuric acid ≥89.1% Fe precipitated in a form of chemically pure complex salt Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> ·4H<sub>2</sub>SO<sub>4</sub>; ≥99.7% of admixtures remained in solution.

Iron sulfate Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> ·4H<sub>2</sub>SO<sub>4</sub> was filtered on a vacuum filter, filtrate was used in the Precipitation II stage, and the salt was decomposed at a temperature 600-700°C for 1 hour. The formed gas SO<sub>3</sub> and sulfuric acid vapor were applied to precipitate iron salts, admixtures, and to produce sulfuric acid for sale in accordance with the given technological scheme. The product obtained after calcination contained ≥99.7% of Fe<sub>2</sub>O<sub>3</sub>, by its physical and chemical properties it was iron-oxide pigment of high quality. This product can be used both for the production of the high quality iron powder and various iron compounds (Fe<sub>3</sub>O<sub>4</sub> etc.). The filtrate after Precipitation I contained 42% H<sub>2</sub>SO<sub>4</sub>; 21.6 g/l Fe. At stage Precipitation II it was saturated with SO<sub>3</sub> gas to a concentration of sulfuric acid in solution equal to 43.2%, the iron content in solution decreased to 7.7g/l. A portion of admixtures, about 2% of the total amount in the raw material, was precipitated together with iron (III) sulfate

crystals. The crystals were filtered and then used in Precipitation I, and the solution containing admixtures was forwarded to precipitation III.

Precipitation III was also performed with SO<sub>3</sub>. Precipitation III was also performed with SOO solution equal to 43.2%, the iron content in solution decreased to 7.7g/l. A portion of admixtures, about 2% of the total amount in the raw material, was precipitated together with iron (III) sulfate crystals. Precipitation III was also performed with SOO solution equal to 43.2%, the iron content in solution decreased to 7.7g/l. A portion of admixtures, about 2% of the total amount in the raw material, was precipitated together with iron (III) sulfate crystals. Precipitation III was also performed with SOO solution equal to 43.2%, the iron content in solution decreased to 7.7g/l. A portion of admixtures, about 2% of the total amount in the raw material, was precipitated together with iron (III) sulfate crystals.

**Comparative Example 2.**

Under conditions of example 1, one weight portion of sulfide waste was mixed with 0.72 weight portions of 98.3% H<sub>2</sub>SO<sub>4</sub>, that was 80% of the theoretically required amount of sulfuric acid. After sulfatization about 70% of iron yielded to solution.

**Example 3.**

Under conditions of example 1, one weight portion of sulfide waste was mixed with 1.1 weight portions of 98.3% H<sub>2</sub>SO<sub>4</sub> (120% of the theoretically required amount). The iron yield to solution was 95%.

**Comparative Example 4.**

Under conditions of example 1, sulfatization was performed at a temperature 250°C. The yield of iron in solution was 66%.

**Example 5.**

Under conditions of example 1, sulfatization was performed at a temperature 350°C. The yield of iron in solution was 95%.

**Example 6.**

Under conditions of example 1, the sulfatization was performed at the air amount equal to 100% of the stoichiometric amount. Elementary sulfur and SO<sub>2</sub> were formed, about 30% of iron was in its bivalent form.

**Comparative Example 7.**

Under conditions of example 1, leaching of the sulfatization product was made in 2% sulfuric acid solution (20g/l H<sub>2</sub>SO<sub>4</sub>). The yield of iron to solution was 70%.

**Example 8.**

Under conditions of example 1 leaching was made in solution of 5% sulfuric acid. The yield of iron to solution was 94.5%.

**Example 9.**

Under conditions of example 1, leaching was made in 35% sulfuric acid solution. The yield of iron to solution was 94.8% because of the partial precipitation of iron sulfate.

**Comparative Example 10.**

Under conditions of example 1, precipitation of iron sulfate was performed by saturation of the solution with SO<sub>3</sub> gas up to H<sub>2</sub>SO<sub>4</sub> concentration equal to 40%. Iron yield in pure crystals was 75%.

**Example 11.**

Under conditions of example 1 precipitation of iron sulfate was made by saturation of the solution with gas SO<sub>3</sub> up to a sulfuric acid concentration 45%. Iron yield in crystals increased to 93%, however, Fe<sub>2</sub>O<sub>3</sub> obtained from these crystals and contained 98% of Fe<sub>2</sub>O<sub>3</sub> and 2% of oxides of other metals.

It will be evident to those skilled in the art that the invention is not limited to the details of the foregoing illustrative examples and that the present invention may be embodied in other specific forms without departing from the essential attributes thereof, and it is therefore desired that the present embodiments and examples be considered in all respects as illustrative and not restrictive, reference being made to the appended claims, rather than to the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.